Version 1.0: 02/2010

General Certificate of Education

# Chemistry 2421

## CHEM4 Kinetics, Equilibria and Organic Chemistry

# Mark Scheme

*2010 examination - January series*

Mark schemes are prepared by the Principal Examiner and considered, together with the relevant questions, by a panel of subject teachers. This mark scheme includes any amendments made at the standardisation meeting attended by all examiners and is the scheme which was used by them in this examination. The standardisation meeting ensures that the mark scheme covers the candidates' responses to questions and that every examiner understands and applies it in the same correct way. As preparation for the standardisation meeting each examiner analyses a number of candidates' scripts: alternative answers not already covered by the mark scheme are discussed at the meeting and legislated for. If, after this meeting, examiners encounter unusual answers which have not been discussed at the meeting they are required to refer these to the Principal Examiner.

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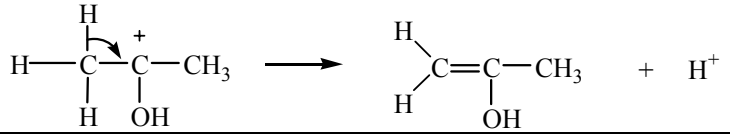
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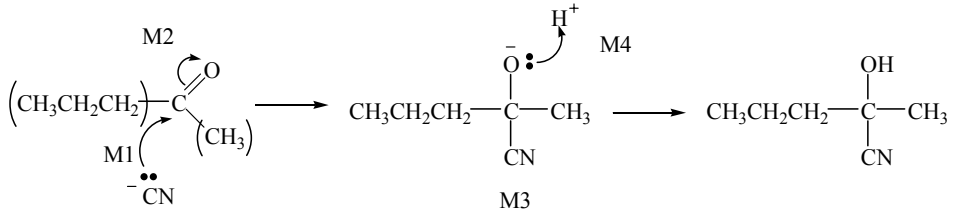
| Question | Part | Sub part | | Mark | Comments |
|---|---|---|---|---|---|
| 1 | (a) | (i) | acid 0.46<br>alcohol 1.46<br>water 5.54 | 1<br>1<br>1 | |
| 1 | (a) | (ii) | $K_c = \frac{[CH_3CH_2COOCH_2CH_3][H_2O]}{[CH_3CH_2COOH][CH_3CH_2OH]} = \frac{[ester][water]}{[acid][alcohol]}$ | 1 | penalise ( )<br>allow molecular formulae or minor slip in formulae |
| 1 | (a) | (iii) | $\frac{(0.54/V)(5.54/V)}{(0.46/V)(1.46/V)}$ Allow without V<br>4.45 or 4.5<br>cancel (as equal no of moles on each side of equation) | 1<br>1<br>1 | Conseq on values in (a)(i)<br>If values used wrongly<br>or wrong values inserted<br>or wrong Kc no marks for calc<br>Part 1(a)(iii) for info 0.46 × 1.46 = 0.6716<br>Possible wrong answers<br>acid 0.46 √ / alcohol 1.46 √ / water 4.46 X → gives Kc = 3.59 √√<br>acid 0.46 √ / alcohol 1.46 √ / water 0.54 X → gives Kc = 0.434 √√ |
| 1 | (b) | (i) | decrease or be reduced or fewer | 1 | |
| 1 | (b) | (ii) | decrease or be reduced or less time or faster or quicker | 1 | |
| 1 | (b) | (iii) | decrease or be reduced | 1 | |

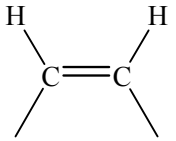
| Question | Part | Sub part | | Mark | Comments |
|---|---|---|---|---|---|
| 2 | (a) | (i) | $-\log[H^+]$ | 1 | or $\log 1/[H^+]$ penalise ( ) |
| 2 | (a) | (ii) | $[H^+] = 0.56$<br><br>$[H_2SO_4] = ½ \times 0.56 = 0.28$ | 1<br><br>1 | mark for the answer; allow 2dp or more |
| 2 | (b) | (i) | $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$<br><br>***OR***<br><br>$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$ | 1 | Allow $CH_3CO_2H$ etc |
| 2 | (b) | (ii) | mol acid = $(25.0 \times 10^{-3}) \times 0.41 = 1.025 \times 10^{-2}$ or $1.03 \times 10^{-2}$<br><br>[NaOH] = $1.025 \times 10^{-2} / 22.6 \times 10^{-3} = 0.45(4)$<br><br>***OR***<br><br>[NaOH] = $1.03 \times 10^{-2} / 22.6 \times 10^{-3} = 0.456$ or 0.46 | 1<br><br>1 | <br><br>mark for answer<br>if not 0.454 look back for error |
| 2 | (b) | (iii) | cresol purple | 1 | |
| 2 | (b) | (iv) | NaOH reacts with <u>carbon dioxide</u> (in the air) | 1 | |
| 2 | (c) | (i) | $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ allow molecular formulae or minor slip in formulae | 1 | penalise ( )<br>allow $H_3O^+$<br>not allow HA etc |

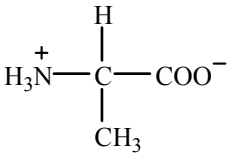
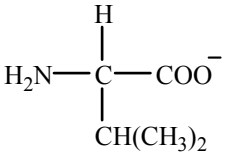
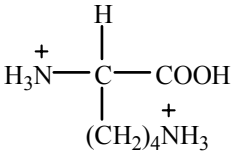
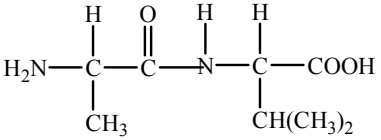
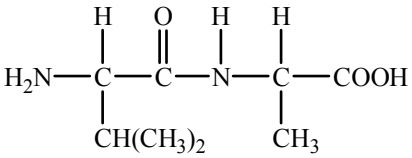
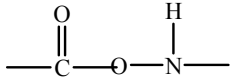
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|---|---|---|---|---|---|
| 2 | (c) | (ii) | $K_a = \frac{[H^+]^2}{[CH_3COOH]}$ or with numbers<br><br>$[H^+] = (\sqrt{(1.74 \times 10^{-5} \times 0.410)} = \sqrt{(7.13 \times 10^{-6})}) = 2.67 \times 10^{-3}$<br><br>pH = 2.57 can give three ticks here for (c)(ii)<br>penalise decimal places < 2 > | 1<br><br>1<br><br>1 | allow HA etc here<br>This can be scored in part(c)(i) but doesn't score there.<br><br>mark for $2.67 \times 10^{-3}$ or $2.7 \times 10^{-3}$ either gives 2.57<br><br>pH mark conseq on their $[H^+]$<br><br>so 5.15 gets 2 marks where square root not taken |

| | | | | | |
|---|---|---|---|---|---|
| **2** | (c) | (iii) | **M1** mol $OH^-$ = $(10.0 \times 10^{-3}) \times 0.10 = 1.0 \times 10^{-3}$<br><br>**M2** orig mol HA = $(25.0 \times 10^{-3}) \times 0.41 = 0.01025$<br>or $1.025 \times 10^{-2}$ or $1.03 \times 10^{-2}$<br>**M3** mol <u>HA</u> in buffer = orig mol HA – mol $OH^-$<br>= 0.00925 or 0.0093<br><br>**M4** mol $A^-$ in buffer = mol $OH^-$ = $1.0 \times 10^{-3}$<br><br>**M5** $[H^+] = (\frac{Ka \times [CH_3COOH]}{[CH_3COO^-]} = )$<br>$\frac{(1.74 \times 10^{-5})(0.00925)}{0.0010}$ or $\frac{(1.74 \times 10^{-5})(0.00930)}{0.0010}$<br><br>$(= 1.61 \times 10^{-4}$ or $1.62 \times 10^{-4})$<br><br>**M6** pH = 3.79 can give six ticks for 3.79<br><br>NB Unlike Qu 2(c)(ii), this pH mark is NOT awarded conseq to their $[H^+]$ unless following AE | 1<br><br>1<br><br>1<br><br>1<br><br>1<br><br>1 | If no subtraction or other wrong chemistry the max score is 3 for M1, M2 and M4<br><br>If $A^-$ is wrong, max 3 for M1, M2 and M3<br>or use of pH = pKa – log [HA]/ $[A^-]$<br><br>Mark is for insertion of correct numbers in correct expression for $[H^+]$<br><br>if [HA]/[ $A^-$ ] upside down lose M5 & M6<br><br>If wrong method e.g. $[H^+]^2/[HA]$<br>max 3 for M1, M2 and M3<br><br>Some may calculate concentrations<br>[HA] = 0.264 and $[A^-]$ = 0.0286 and rounding this to 0.029 gives pH = 3.80 (which is OK)<br><br>BEWARE: using 0.01025 wrongly instead of 0.00925 gives pH = 3.75<br>(this gets 3 for M1, M2 & M4) |

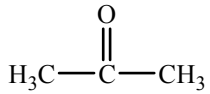
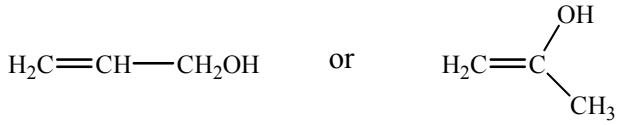
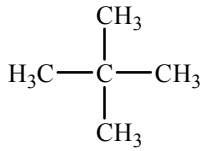
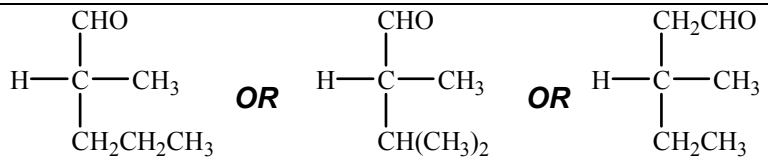
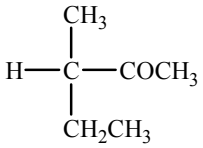
| Question | Part | Sub Part | | Mark | Comment |
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| 3 | (a) | | 2 or two or second | 1 | |
| 3 | (b) | | $k = \frac{1.24 \times 10^{-4}}{(4.40)(0.82)}$<br><br>$= 3.44 \times 10^{-5}$ (min 3sfs)<br><br>$mol^{-1}dm^3s^{-1}$ | 1<br><br>1<br><br>1 | mark is for insertion of numbers into a correctly rearranged rate equ , k = etc<br>if upside down, (or use of $I_2$ data) score only units mark<br><br>any order |
| 3 | (c) | | no change or no effect or stays the same or $1.24 \times 10^{-4}$ | 1 | |
| 3 | (d) | | 1 or 2 or 1 and 2<br><br>rate equ doesn't involve $I_2$ or only step which includes 2 species in rate equ | 1<br><br>1 | if wrong no further mark<br>but mark on from no answer |
| 3 | (e) | |  | 1 | any second arrow loses the mark |

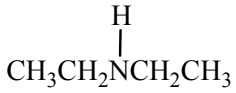
| Question | Part | Sub Part | | Mark | Comments |
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| 4 | (a) | | nucleophilic addition<br><br><br>M3 for completely correct structure not including lp<br>M4 for lp and arrow<br>2-hydroxy-2-methylpentan(e)nitrile | 1<br><br><br>4<br><br><br><br><br><br>1 | Attack by HCN loses M1 and M2<br>M2 not allowed independent of M1, but<br>allow M1 for correct attack on C+<br>+C=O loses M2<br>M2 only allowed if correct carbon attacked<br>allow minus charge on N i.e. :$CN^-$<br>allow $C_3H_7$ in M3<br><br>allow without –<br>allow 2-hydroxy-2-methylpentanonitrile |
| 4 | (b) | | Product from **Q** is a racemic mixture/ equal amounts of enantiomers<br>racemic mixture is inactive or inactive explained<br>Product from **R** is inactive (molecule) or has no chiral centre | 1<br><br><br>1<br><br><br>1 | if no reference to products then no marks;<br>not **Q** is optically active or has a chiral centre etc |
| 4 | (c) | (i) | **mark the three sections of Qu 4(c) separately**<br>**R** or $CH_3CH_2COCH_2CH_3$ | 1 | |
| 4 | (c) | (ii) | $[CH_3CH_2COCH_2CH_3]^{+\cdot}$ ***OR*** $[C_5H_{10}O]^{+\cdot}$<br>$\rightarrow$ $[CH_3CH_2CO]^+ + {}^{\cdot}CH_2CH_3$<br>***OR*** $\rightarrow$ $[C_3H_5O]^+ + {}^{\cdot}C_2H_5$ | 1<br><br><br>1 | allow molecular formulae<br>allow without brackets<br>if brackets not shown, allow dot anywhere on radical or + anywhere on ion |
| 4 | (c) | (iii) | m/z = 43 or 71 | 1 | |

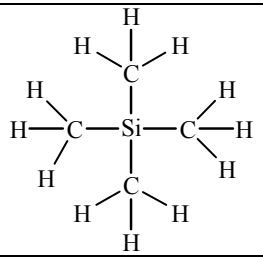
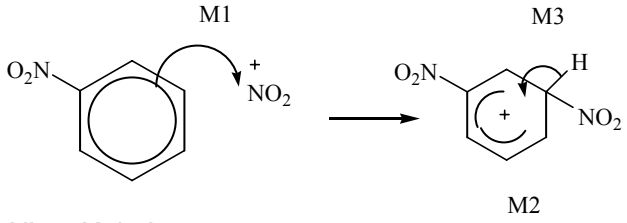
| Question | Part | Sub Part | | Mark | Question |
|---|---|---|---|---|---|
| 5 | (a) | (i) | propan(e)-1,2,3-triol or 1,2,3- propan(e)triol | 1 | not propyl<br>ignore hyphen, commas |
| 5 | (a) | (ii) | soaps | 1 | allow anionic surfactant<br>not cationic surfactant<br>not detergents, not shampoos |
| 5 | (b) | (i) | (bio)<u>diesel</u> | 1 | Allow fuel for <u>diesel</u> engines<br>not biofuel, not oils |
| 5 | (b) | (ii) |  | 1 | ignore anything else attached except any more H atoms. |
| 5 | (b) | (iii) | $CH_3(CH_2)_{12}COOCH_3 + 21½\ O_2 \rightarrow 15CO_2 + 15\ H_2O$<br>***OR***<br>$C_{15}H_{30}O_2$ or 43/2 | 1 | **not** allow equation doubled |

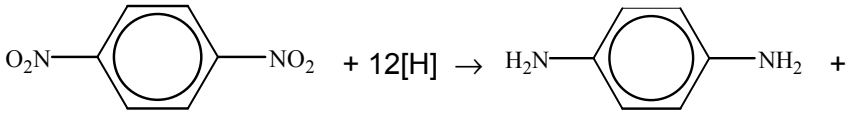
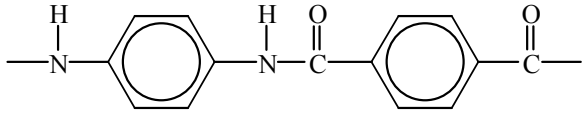
| Question | Part | Sub Part | | Mark | Comments |
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| 6 | (a) | (i) |  | 1 | allow $-CO_2^-$<br>allow $^+NH_3-$<br>don't penalize position of + on $NH_3$ |
| 6 | (a) | (ii) |  | 1 | allow $-CO_2^-$<br>allow $NH_2-$<br>allow $C_3H_7$ |
| 6 | (a) | (iii) |  | 1 | allow $-CO_2H$<br>allow $^+NH_3-$<br>don't penalize position of + on $NH_3$ |
| 6 | (b) | | <br> | 1<br><br><br><br><br>1 | allow $-CO_2H$<br>allow $NH_2-$<br>allow $C_3H_7$<br>allow as zwitterions<br>if error in peptide link e.g.<br><br>if twice, penalise both times<br>not polymers<br>if wrong amino acid in both can score Max 1 |

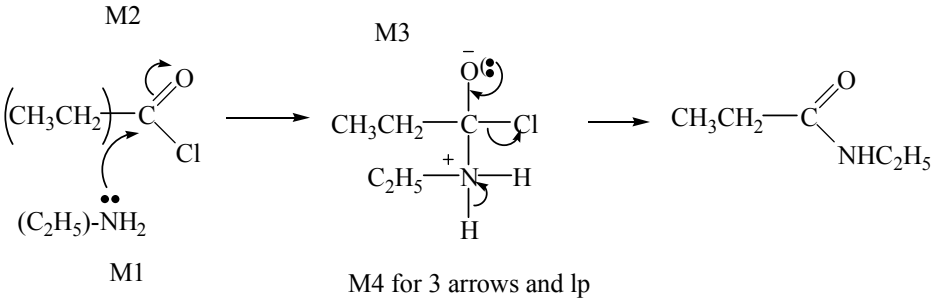
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| 6 | (c) | | chromatography or electrophoresis | 1 | ignore qualification to chromatography |

| Question | Part | Sub Part | | Mark | Comments |
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| 7 | (a) | | A  | 1 | allow $CH_3COCH_3$ |
| | | | B  | 1 | must show C=C<br>Penalise sticks once per pair |
| 7 | (b) | | C $CH_3CH_2CH_2CH_2CH_3$ | 1 | |
| | | | D  | 1 | NOT cyclopentane which is only $C_5H_{10}$<br>Penalise sticks once per pair |
| 7 | (c) | | E $CH_3CH_2COOCH_3$ | 1 | Allow $C_2H_5CO_2CH_3$ |
| | | | F $CH_3COOCH_2CH_3$ | 1 | Allow $CH_3CO_2CH_2CH_3$ or $CH_3CO_2C_2H_5$<br>Penalise sticks once per pair |
| 7 | (d) | | G <br>allow $C_3H_7$ allow $C_3H_7$ allow $C_2H_5$ | 1 | not $C_5H_{11}$ nor $C_4H_9$<br>Penalise sticks once per pair |
| | | | H <br>allow $C_2H_5$ | 1 | |

| | | | | | |
|---|---|---|---|---|---|
| 7 | (e) | | I  | 1 | allow $C_2H_5$ |
| | | | J  | 1 | NOT $C_3H_7$<br>Penalise sticks once per pair |

| Question | Part | Sub Part | | Mark | Comments |
|---|---|---|---|---|---|
| (8) | (a) | (i) | **W** 3<br><br>**X** 4<br><br>**Y** 2 | 1<br><br>1<br><br>1 | |
| (8) | (a) | (ii) |  | 1 | displayed formula shows ALL bonds |
| (8) | (b) | (i) | $NO_2^+$<br><br>$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$<br><br>***OR***<br><br>$HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$ | 1<br><br>1 | allow + anywhere<br>can score in equation<br>or use two equations via $H_2NO_3^+$ |
| (8) | (b) | (ii) | electrophilic substitution<br><br><br><br>Allow Kekule structures<br>+ must be on N of $^+NO_2$ (which must be correct)<br>both $NO_2$ must be correctly positioned and bonded to gain M2 | 1<br><br>3 | Not Friedel Crafts<br><br>M1 arrow from circle or within it to N or to + on N<br>horseshoe must not extend beyond C2 to C6 but can be smaller<br>+ not too close to C1<br>M3 arrow into hexagon unless Kekule<br>allow M3 arrow independent of M2 structure<br>ignore base removing H in M3 |

| | | | | | |
|---|---|---|---|---|---|
| 8 | (c) | (i) | $H_2$/Ni or $H_2$/Pt or Sn/HCl or Fe/HCl (conc or dil or neither) allow dil $H_2SO_4$<br>ignore mention of NaOH<br><br>$4H_2O$<br>Or $6H_2$ | 1<br><br><br><br>1 | Not $NaBH_4$ Not $LiAlH_4$ Not $Na/C_2H_5OH$<br>not conc $H_2SO_4$ or any $HNO_3$<br><br><br>allow $C_6H_4(NO_2)_2$ etc ,<br>allow $NO_2$– $NH_2$–<br>i.e. be lenient on structures, the mark is for balancing equ |
| 8 | (c) | (ii) | <br>1st mark for correct peptide link<br>2nd mark for the rest correct including trailing bonds | <br><br><br>2 | allow –CONH-<br><br>ignore [ ]n as in polymer |
| 8 | (c) | (iii) | **M1** Kevlar is <u>biodegradeable</u> but polyalkenes not<br>**M2** Kevlar has <u>polar</u> bonds / is a (poly) amide / has peptide link<br>**M3** can be hydrolysed/attacked by nucleophiles/acids/bases/enzymes<br>**M4** polyalkenes <u>non polar</u> /has <u>non-polar</u> bonds | 1<br>1<br>1<br>1 | allow Kevlar is <u>more</u> biodegradeable<br>comment on structure of Kevlar<br><br>comment on structure of polyalkenes but not just strong bonds |

| Question | Part | Sub Part | | Mark | Comments |
|---|---|---|---|---|---|
| 9 | (a) | | (nucleophilic) addition-elimination | 1 | |
| | | | <br>M4 for 3 arrows and lp | 4 | minus on $NH_2$ loses M1<br>M2 not allowed independent of M1, but<br>allow M1 for correct attack on C+<br>+C=O loses M2<br>only allow M4 after correct or very close M3<br>lose M4 for $Cl^-$ removing $H^+$ in mechanism, but ignore HCl as a product |
| | | | <u>N-ethylpropanamide</u> | 1 | Not N-ethylpropaneamide |
| 9 | (b) | | $CH_3CN$ or ethan(e)nitrile or ethanonitrile | 1 | not ethanitrile<br>but allow correct formula with ethanitrile |
| | | | for each step wrong or no reagent loses condition mark | 1 | contradiction loses mark |
| | | | Step 1 $Cl_2$ | | |
| | | | uv or above 300 $^oC$ | 1 | wrong or no reagent loses condition mark |
| | | | Step 2 KCN | 1 | |
| | | | aq and alcoholic (both needed) | 1 | allow uv light / (sun)light / uv radiation |
| | | | Step 3 $H_2$/Ni or $LiAlH_4$ or $Na/C_2H_5OH$ | 1 | not $CN^-$ but mark on<br>NOT HCN or KCN + acid, and this loses condition mark<br>NOT $NaBH_4$ Sn/HCl (forms aldehyde!)<br>ignore conditions |